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Pressure dependence of Gruneisen ratio of MgO at high temperatures

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Abstract : In the present communication, a simple approach is established to predict dependence of Gruneisen ratio of MgO in high temperature domain. The calculations are shown with the help of more accurate input data, suggested by Jacobs and Oonks [*Phys. Chem. Chem. Phys.* **2** 2641 (2000)]. The predicted values of compression dependence of the Gruneisen parameter are compared with those evaluated by Cynn *et al* [*J. Phys. Chem.* **99** 7813 (1995)]. The Vinet equation of state (EoS) is used to convert compression to corresponding pressure. It is found that the Gruneisen parameter decreases with compression along an isotherm. The present analysis is useful to study the anharmonic properties of MgO.

Keywords : Gruneisen ratio, equation of state, MgO.

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1. Introduction

The Gruneisen ratio (γ) is a very important parameter used to quantify the relationship between thermal and elastic properties of solids. γ can be considered as the measure of the change of pressure resulting from the increase of energy density at constant volume V. The γ is one of the important quanta which characterize the anharmonic properties of solids. Many theoretical models [1–5] have been established to calculate the Gruneisen ratio, and the relation between the Gruneisen parameter and volume, or the pressure.

In the present study, an approach to calculate γ of a simple oxide (MgO) at high temperatures and pressures is described. MgO is used to demonstrate this computational method because it is regarded as the second major component (next to $MgSiO_3$ perovskite) of the Earth lower mantle. The wide range of stability of MgO throughout pressure-temperature space also makes it attractive for study. This work is motivated by the calculations of γ of MgO by Anderson *et al* [6] for a wide range in pressure-temperature space, based on the relationship

$$\gamma = \frac{\alpha K_T V}{C_V} \tag{1}$$

where α is the thermal expansivity, K_T is the isothermal bulk modulus, and C_V is the heat capacity at constant volume. They evaluated γ by solving separately for the volume dependence of αK_T and C_V. Cynn *et al.* [7] calculated Gruneisen parameter of MgO from the calculation of entropy. Their study was the first to calculate the γ through adiabatic lapse rate. Here, the calculations on γ for solid under consideration are done with the help of the more accurate data suggested by Jacobs and Oonks [8] which can be considered more accurate. The method of analysis is shown on Section 2. Results are discussed in Section 3.

2. Method of analysis

It is shown by Anderson and coworkers [9,10] on the basis of investigation made by Chopelas and Boehler [11,12] that the Anderson-Gruneisen parameter $\delta(T, P)$ is not independent of pressure or compression and investigated the following relationship

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$$\frac{\delta(T,P)}{\delta(T,0)}\left[\frac{V(T,P)}{V(T,0)}\right]^{k}=\eta^{k} \tag{2}$$

where k is a dimensionless thermo-elastic parameter and $\eta=[V(T,P)/V(T,0)]$. Using eq. (2), Anderson and Isaak [10] obtained following relationship for compression (η) dependence of thermal expansivity

$$\alpha(T,P)=\alpha(T,0)\exp\left[-\frac{\delta(T,0)}{k}\left(1-\eta^{k}\right)\right], \tag{3}$$

where the symbols have their usual meaning. Eq. (3) provides a method for determining thermal expansivity at various compressions along several isotherms. The results obtained by the Anderson-Isaak equation (eq. (3)) for thermal expansivity at different compressions along isotherms have been found [13–15] to present good agreement with the experimental data [16,17] as well as with the results based on first principle calculations for MgO [18].

From shock wave and static compression measurements on a variety of metals, Grover *et al* [19] found a linear relationship between the logarithm of bulk modulus and the volume up to volume change of 40%. Following the work of Grover *et al* [19], we can write a relationship for pressure dependence of isothermal bulk modulus $K(T,P)$, as

$$K(T,P)=K(T,0)\exp\left[K'(T,0)\{1-\eta\}\right], \tag{4}$$

where $K'(T,0)$ is the first pressure derivative of the isothermal bulk modulus. The results obtained from eq. (4) for MgO are in good agreement with the experiments [18–20]. Multiplication of eqs. (3) and (4), results following relationship for pressure (compression) dependence of αK_T along an isotherm

$$\alpha(T,P)K(T,P)=\alpha(T,0)K(T,0)\times\exp\left[K'(T,0)\{1-\eta\}-\frac{\delta(T,0)}{k}\left(1-\eta^{k}\right)\right]. \tag{5}$$

Now, if one assumes that C_V is constant [21] in high temperature and pressure domain, then eq. (1) yields following relationship for the pressure dependence of Gruneisen ratio

$$\frac{\gamma(T,P)}{\gamma(T,0)}=\frac{\alpha(T,P)K(T,P)}{\alpha(T,0)K(T,0)}. \tag{6}$$

Combination of eq. (5) and eq. (6) results following relationship to compute the pressure dependence of Gruneisen ratio in high temperature region along an isotherm

$$\gamma(T,P)=\gamma(T,0)\eta\exp\left[K'(T,0)\{1-\eta\}-\frac{\delta(T,0)}{k}\left(1-\eta^{k}\right)\right]. \tag{7}$$

3. Results and discussion

Table 1 shows the input parameters (at $P=0$) used in computation of the pressure dependence of the Gruneisen

Table 1. Input parameters used in calculations all at $P=0$.

T	$a\times10^5$ K	(V/V_0)	V_m/cm^3	C_P(JK^{-1})	K_S(GPa)	K_T(GPa)	γ	δ_T	K'_0	k
300	3.1741	1.0000	11.2507	37.105	163.93	161.50	1.5777	5.969	4.77	1.41
400	3.5497	1.0034	11.2887	42.475	162.33	158.88	1.5314	5.426	4.79	1.34
500	3.7904	1.0071	11.3303	45.571	160.73	156.25	1.5147	5.167	4.80	1.39
600	3.9663	1.0110	11.3744	47.521	158.87	153.37	1.5082	5.030	4.82	1.40
700	4.1071	1.0151	11.4204	48.848	157.11	150.38	1.5086	4.954	4.84	1.45
800	4.2280	1.0193	11.4681	49.818	155.10	147.57	1.5096	4.904	4.86	1.52
900	4.3372	1.0237	11.5174	50.576	153.06	144.53	1.5118	4.882	4.88	1.50
1000	4.4398	1.0282	11.5680	51.207	151.07	141.55	1.5152	4.869	4.90	1.48
1100	4.5388	1.0328	11.6201	51.765	148.91	138.42	1.5172	4.871	4.93	1.44
1200	4.6366	1.0376	11.6735	52.280	146.69	135.26	1.5187	4.879	4.95	1.44
1300	4.7344	1.0425	11.7283	52.776	144.42	132.07	1.5195	4.894	4.97	1.46
1400	4.8334	1.0475	11.7846	53.266	142.03	128.79	1.5188	4.916	5.00	1.39
1500	4.9343	1.0526	11.8423	53.759	139.68	125.57	1.5183	4.939	5.02	1.39
1600	5.0377	1.0578	11.9015	54.262	137.31	122.35	1.5172	4.965	5.05	1.38
1700	5.1440	1.0632	11.9622	54.780	134.94	119.15	1.5158	4.993	5.07	1.32
1800	5.2537	1.0688	12.0245	55.316	132.74	116.10	1.5159	5.017	5.10	1.31

parameter at high temperature. The thermal expansivity data listed in Table 1 are outcome of an optimization procedure, in which data from various sources [22–28] were weighed and combined for maximum mutual consistency and thermodynamic stability. These data are suggested by Jacobs and Oonks [8] and can be considered the more accurate for the present study. Data for K_S are taken from Isaak *et al* [29]. Values of molar volumes (V_m) at different temperatures for solid under consideration are computed through thermal expansivity data. The isothermal bulk modulus (K_T) and C_P are calculated through thermodynamic relationships [8]. Values of dimensionless thermoelastic parameter (k), are extracted from literature [7,29]. Values of temperature dependence of Gruneisen ratio (γ) at atmospheric pressure are calculated through $\gamma = \alpha K_S V/C_P$ and listed in Table 1 along the input data. Temperature dependence of the Anderson-Gruneisen parameter (δ_T) are evaluated by the mathematical definition of the parameter as given below :

$$\delta_T = -\frac{1}{\alpha K_T}\left(dK_T/dT\right)_P, \tag{8}$$

where $\left(dK_T/dT\right)_P = -0.0306$ K^{-1}GPa for the solid under consideration which is the outcome of the close analysis of data on K_T. Values of temperature dependence of the first pressure derivative of the isothermal bulk modulus at zero pressure (K_T') enlisted in the second last column of Table 1 are calculated by the following relationship [8]

$$K_T' = -\frac{1}{} \tag{9}$$

where $b = -2.359\times10^{-6}$ m^3 $mole^{-1}$.

Table 2 shows the pressure dependence of Gruneisen ratio computed through eq. (7) using input parameters from Table 1 in high temperature domain. At ambient condition, Isaak *et al* [29] calculated γ from RPR measurements of K_S and thermal expansion data. Their best estimate for $\gamma = 1.54 \pm 0.08$ is essentially identical to the value calculated in present study 1.5777. Values of $\gamma(T,\eta)$ calculated through present study, are compared to those evaluated by Cynn *et al* [7] with the help of adiabatic lapse rate and entropy. Comparison of $\gamma(T,\eta)$ in Table 2 shows that $\gamma(T,\eta)$ recommended by present study are slightly higher than those recommended by

Table 2. Predicted values of compression dependence of Gruneisen ratio along several isotherms in high temperature region and compared with those calculated by Cynn *et al* [7] shown in parenthesis.

($\eta\downarrow/T\rightarrow$)	900 K	1000 K	1100 K	1200 K	1300 K	1400 K	1500 K	1600 K	1700 K	1800 K
1.00	1.5117	1.5152	1.5172	1.5187	1.5195	1.5188	1.5183	1.5172	1.5158	1.5159
		(1.5400)					(1.5170)			
0.95	1.4406	1.4448	1.4493	1.4517	1.4533	1.4521	1.4518	1.4506	1.4486	1.5136
		(1.4230)					(1.4060)			
0.90	1.3776	1.3821	1.3881	1.3915	1.3941	1.3914	1.3912	1.3898	1.3862	1.5132
		(1.3190)					(1.3080)			
0.85	1.3218	1.3263	1.3331	1.3372	1.3412	1.3360	1.3359	1.3342	1.3281	1.5144
		(1.2290)					(1.2200)			
0.80	1.2723	1.2764	1.2833	1.2882	1.2938	1.2851	1.2852	1.2831	1.2738	1.5170
		(1.1510)					(1.1410)			
0.75	1.2282	1.2317	1.2380	1.2436	1.2511	1.2380	1.2384	1.2357	1.2225	1.5205
		(1.0860)					(1.0730)			
0.70	1.1887	1.1914	1.1965	1.2029	1.2124	1.1942	1.1949	1.1916	1.1738	1.5245
		(1.0310)					(1.0130)			
0.65	1.1530	1.1546	1.1581	1.1651	1.1768	1.1530	1.1538	1.1498	1.1270	1.5283
		(0.9850)					(0.9600)			
0.60	1.1202	1.1206	1.1219	1.1296	1.1437	1.1135	1.1146	1.1099	1.0814	1.5310
		(0.9500)					(0.9130)			
0.55	1.0893	1.0883	1.0870	1.0953	1.1120	1.0748	1.0763	1.0707	1.0364	1.5316
0.50	1.0592	1.0566	1.0523	1.0612	1.0806	1.0361	1.0378	1.0315	0.9909	1.5284
0.45	1.0284	1.0242	1.0166	1.0260	1.0481	0.9961	0.9981	0.9909	0.9440	1.5195
0.40	0.9953	0.9893	0.9781	0.9880	1.0129	0.9532	0.9555	0.9474	0.8943	1.5021

Cynn *et al* [7]. However, in the present study, a direct method is used along with the more accurate data, thus, $\gamma(T,\eta)$ computed here may be considered more accurate than those calculated by Cynn *et al* [7].

The corresponding pressure on a particular compression and temperature can be evaluated by an equation of state (EoS). The Vinet EoS has been found [30–33] to yield good agreement with *ab initio* results upto extremely high pressures corresponding to the compression down to 0.3, which can be expressed as :

$$P = 3K_0(1-x)x^{-2}\exp[y(1-x)], \tag{10}$$

where $x = \eta^{1/3}$ and $y = \frac{3}{2}\left[K'(T,0)-1\right]$, K_0 and K_0' are the values of K_T and (dK_T/dP) respectively, at P = 0. Using the input parameters from Table 1, values of pressure at the corresponding compression are shown in Table 3.

Cui and Chen [5] obtained the following relationship for $\gamma(T,\eta)$

$$\frac{\gamma}{\gamma_0} = \frac{1}{\eta^{K_0'}}\exp[A(\eta-1)], \tag{11}$$

where $A = \delta(T,0)+1$. The above relationship is derived by assuming a linear relationship between the bulk modulus and the pressure and following the work of Chopelas and Boehler [12]. Cui and Chen [5] have shown the validity of eq. (11) for NaCl. Here, an attempt has also been made to predict $\gamma(T,\eta)$ for MgO using eq. (11). The predicted values are listed in Table 4. It is found that $\gamma(T,\eta)$ predicted by eq. (11) differs more from those predicted by eq. (7), especially in high compression regions. Thus, it is recommended that relation (11) should be used in the region of low pressures (compressions), as for the case of NaCl.

The Gruneisen ratio evaluated in the present study,

Table 3. Pressure (GPa) corresponding to different compressions for MgO calculated through Vinet EoS.

($h\downarrow/T\rightarrow$)	900 K	1000 K	1100 K	1200 K	1300 K	1400 K	1500 K	1600 K	1700 K	1800 K
1.00	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.95	8.3953	8.2267	8.0493	7.8701	7.6890	7.5026	7.3196	7.1364	6.9543	6.7809
0.90	19.625	19.242	18.838	18.429	18.016	17.590	17.172	16.754	16.337	15.941
0.85	34.639	33.982	33.289	32.587	31.877	31.144	30.425	29.703	28.985	28.302
0.80	54.750	53.745	52.682	51.604	50.513	49.385	48.278	47.166	46.060	45.009
0.75	81.802	80.352	78.814	77.254	75.672	74.035	72.427	70.812	69.204	67.678
0.70	118.42	116.40	114.25	112.06	109.85	107.55	105.30	103.03	100.77	98.630
0.65	168.43	165.67	162.72	159.73	156.69	153.54	150.43	147.31	144.21	141.26
0.60	237.49	233.77	229.79	225.74	221.62	217.33	213.12	208.88	204.65	200.65
0.55	334.21	329.24	323.89	318.44	312.89	307.10	301.42	295.69	289.97	284.58
0.50	472.07	465.43	458.26	450.94	443.48	435.67	428.01	420.28	412.56	405.30
0.45	672.87	663.99	654.35	644.50	634.44	623.89	613.54	603.06	592.63	582.83
0.40	973.39	961.45	948.43	935.08	921.43	907.06	892.98	878.71	864.49	851.18

Table 4. Calculated values of Gruneisen ratio for MgO through eq. (11).

($h\downarrow/T\rightarrow$)	900 K	1000 K	1100 K	1200 K	1300 K	1400 K	1500 K	1600 K	1700 K	1800 K
1.00	1.5118	1.5152	1.5172	1.5187	1.5195	1.5188	1.5183	1.5172	1.5158	1.5159
0.95	1.4472	1.4530	1.4565	1.4589	1.4604	1.4599	1.4596	1.4585	1.4571	1.4574
0.90	1.4043	1.4124	1.4174	1.4209	1.4231	1.4229	1.4228	1.4219	1.4204	1.4210
0.85	1.3834	1.3940	1.4005	1.4052	1.4082	1.4084	1.4087	1.4079	1.4066	1.4076
0.80	1.3860	1.3993	1.4077	1.4137	1.4177	1.4184	1.4191	1.4187	1.4176	1.4192
0.75	1.4155	1.4319	1.4424	1.4501	1.4552	1.4567	1.4581	1.4581	1.4573	1.4597
0.70	1.4773	1.4976	1.5108	1.5205	1.5273	1.5296	1.5319	1.5326	1.5324	1.5358
0.65	1.5809	1.6061	1.6229	1.6353	1.6442	1.6478	1.6514	1.6530	1.6537	1.6586
0.60	1.7414	1.7734	1.7949	1.8111	1.8230	1.8285	1.8340	1.8371	1.8390	1.8462
0.55	1.9847	2.0261	2.0545	2.0763	2.0926	2.1010	2.1093	2.1148	2.1188	2.1293
0.50	2.3554	2.4110	2.4498	2.4800	2.5032	2.5162	2.5292	2.5385	2.5460	2.5620
0.45	2.9359	3.0140	3.0693	3.1132	3.1477	3.1687	3.1896	3.2056	3.2193	3.2446
0.40	3.8884	4.0044	4.0883	4.1559	4.2104	4.2458	4.2812	4.3098	4.3353	4.3778

are useful to study the high temperature and high pressure anharmonic thermodynamic properties of MgO.

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